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Techniques for Treating Hazardous Wastes to
Remove Volatile Organic Constituents

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TECHNIQUES FOR TREATING HAZARDOUS WASTES
TO REMOVE VOLATILE ORGANIC CONSTITUENTS

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ABSTRACT

This paper discusses the potential for using commercially available treatment techniques to remove VOCs from hazardous waste streams and addresses some of the issues associated with making waste treatment a viable VOC emission control technique for hazardous waste management facilities. It discusses the waste streams of concern because of their volatile constituents and describes potentially applicable treatment techniques. The use of models for treatment process design is described. Finally, the paper discusses treatment cost, treatment residuals and considerations of importance in choosing where in the life cycle of a hazardous waste stream to treat it.

Introduction

Management of hazardous wastes involves numerous operations, many of which can result in air emissions. While small amounts of waste are generally stored in closed-topped tanks and treatment often occurs in closed vessels, large volumes of wastes are often stored in open surface impoundments where they are exposed to the atmosphere. Similarly, waste treatment and disposal is frequently done in surface impoundments, or on land treatment plots where escape to the atmosphere of the waste's volatile constituents may occur rapidly. Disposal of wastes in landfills may release volatile organic compounds (VOCs), although these are usually not as rapid once the landfill is capped. Numerous waste transfer and handling operations may also be a significant source of VOC emissions.

As discussed in another paper presented at this session,¹ there are several ways of controlling emissions from these hazardous waste management operations. "Add-on" (or "end-of-pipe") controls such as flares or carbon canisters can be used to capture or destroy VOC emissions after they have migrated into the gas phase of the system. Other, "in-situ," controls (such as wind barriers or floating rafts) can be used to reduce the rates at which volatile compounds escape from the waste. Both of these categories of pollution control techniques have disadvantages. Capturing pollutants from emission sources of large area can be expensive and may be complicated by such factors as high humidity and mixtures of compounds (which can corrode flares or lead to adsorber breakthrough). "In-situ" controls do not remove the VOCs from the waste stream so there remains the potential for VOC emissions later in the waste handling process.

Treating a waste to reduce its VOC content has a number of important advantages. It is independent of the emissions source and can be used to remove the volatile constituents of the waste stream early in the management cycle. As a result, volatiles are removed at a point where they will generally be in the most concentrated form and where the potential for recycling, if it exists, is greatest.

This paper discusses the potential for using commercially available treatment techniques to remove VOCs from hazardous waste streams and addresses some of the issues associated with making waste treatment a viable VOC emission control technique for hazardous waste management facilities. It discusses the waste streams of concern because of their volatile constituents and describes potentially applicable treatment techniques. The use of models for treatment process design is described. The paper discusses treatment cost, treatment residuals and considerations of importance in choosing where in the life cycle of a hazardous waste stream to treat it. The paper also points out some of the limitations of waste treatment for VOC removal, many of which arise because of the highly variable and complex composition of hazardous waste streams.

This paper is based on a preliminary engineering assessment of hazardous waste treatment as an air pollution control technique^{2,3} on a more recent review of the literature, and on the initial findings of the authors' research on hazardous waste treatment for VOC emissions reduction. Where possible, specific examples from the literature or field testing are cited. The

conclusions presented here are preliminary and research is ongoing to document the usefulness of this approach to air pollution control at hazardous waste treatment, storage and disposal facilities.

Influence of Waste Stream Properties on Treatment Choice

Two factors determine whether the handling of a waste stream may result in significant emissions: (1) whether there is a high potential for VOC emissions from the waste due to its VOC content and other physical and chemical characteristics and/or its high production rate and (2) whether the waste is handled in such a manner that there is a high potential for air emissions. Wastes containing VOCs which are treated and disposed of in surface impoundments, and through land disposal (excluding deep well injection) have a high potential for emissions because these operations have large, exposed surface areas which allow volatilization and are difficult to control. Wastes which are recycled or incinerated should have limited emissions, if proper storage and transfer practices are employed. As a result, wastes with greater than approximately 50 percent organics content are not expected to be of high importance to a VOC removal program and are excluded from consideration here.

The remaining wastes can be broken into three general categories: (1) sludges, (2) aqueous waste streams (i.e. those with less than 10 percent organics in water), and (3) mixed streams (i.e. those with 10-50 percent organics and relatively small amounts of solids).

The amount of organics in an aqueous or mixed stream will determine what types of treatment techniques can be used for the physical separation or for the chemical or biological transformation of volatiles of concern. Figure 1 shows organic concentrations over which various treatment technique are applicable. A solid line approximately indicates the range of organic concentration for which the technique is currently applied commercially. A dashed line indicates where the technique has been applied on selected streams or is undemonstrated, but potentially applicable. Generally, techniques used for organic concentrations over 10 percent are applicable at lower concentrations, but with a significant increase in treatment costs. The extension of techniques which are used for organic concentrations of less than 1 percent (such as wet air oxidation) may also be possible, but there are generally more cost effective techniques available for the higher concentrations.

A second waste stream characteristic--solids content or viscosity--indicates whether the waste will have to be pretreated to remove solids, or operated at elevated temperatures so that it is sufficiently fluid to undergo treatment. Finally, the solubility of the volatile in the waste stream will determine ease of removal by such thermal separation techniques as steam stripping or distillation which are frequently used for mixed or high concentration aqueous streams.

Liquid Stream Treatment Techniques

Liquid stream treatment for organics removal is already commercially practiced, and similar treatment processes will likely be applicable to hazardous waste streams. Aqueous streams with low (<1000 ppm) organic contents can be treated with techniques used in purifying drinking water⁵ or

in municipal wastewater treatment,⁶ as long as air emissions are properly controlled. These techniques are already being used to clean leachate at land disposal sites.⁷ Highly concentrated liquid streams can be treated with techniques used for solvent recycling. However, it is liquid streams of intermediate organic content (0.1-10 percent) and sludges which typically release much of the emissions at hazardous waste management facilities and are most difficult to treat.

This section describes the types of waste streams to which an individual liquid waste treatment technique can be applied and discusses the advantages and disadvantages of each technique.

Stripping

Stripping can be used to remove dissolved volatiles from free flowing liquid streams. For aqueous streams with low (<1 percent) concentrations of compounds of high volatility (Henry's Law constant $\times 10^{-4}$ atm-m³/g-mole) air stripping will likely be applicable.² The air stripping units themselves have the advantage of being inexpensive, since they employ equipment of simple design which is easy to operate. However, the stripper offgases must be treated to minimize air pollution, and this significantly adds to the treatment cost if a unit such as a gas-phase carbon adsorber/regenerator is needed. Some large waste management facilities are minimizing the additional cost of offgas cleanup by using this air stream as part of the combustion air in the facility boiler or waste incinerator. Whatever the mode of stripper-gas cleanup, safety considerations favor the use of a continuous stripper, since the concentrations of VOCs in the offgases of a batch process will vary with time and may enter the explosive concentration range at some time during treatment.

Steam stripping by direct injection of live steam can be used to treat aqueous and mixed wastes containing organic compounds which are at higher concentrations and/or which have lower volatility than those streams which are air strippable. For this reason, steam stripping is used by some waste recyclers for recovery of organics, including volatile species. Therefore, there may be the additional benefit of economic credits from the resale of offgases collected during treatment for VOC emissions control.

There are several disadvantages to steam stripping, however. First, there will be an increased volume of treated aqueous (or mixed) waste to be managed in later process steps because of the addition of steam to the waste. Second, while steam stripper apparatus is of simple design and is relatively inexpensive, it is energy intensive; the cost of steam can account for a major portion of the operating costs for a unit.² These disadvantages will limit the applicability of steam stripping as a VOC removal technique; treatment of aqueous streams to reduce organic concentrations below 1 percent can require multiple passes through a batch stripper without distillation or may lead to even larger volumes of hazardous waste than were present originally.

Steam stripping by direct steam injection does have advantages over other treatment techniques used for mixed streams. It can handle solids in the waste which may foul a heat exchange surface. It can also handle waste streams of more variable composition than can a distillation unit. The treatment temperature is generally lower than for thin film evaporators which is an advantage with volatiles that react or decompose. For these reasons, steam stripping may be useful as an initial VOC removal technique, which could

then be followed by additional treatment to reduce the concentration of VOCs to an acceptable level.

Solvent extraction is used in combination with steam stripping to remove materials such as phenols from waste streams.⁸ A solvent is generally chosen that has low aqueous solubility and a strong affinity for the VOCs contained in the waste. The solvent in the treated waste is removed by steam stripping, and the solvent can be regenerated by distillation. The use of solvent extraction would probably be limited to onsite treatment.

Evaporation

Agitated thin film evaporation is widely used in the waste recycling industry today. While its application is primarily for the separation of low boilers and solids from organic streams, it can be used with mixed streams if the relative volatility of VOC to other stream components is high. Treatment to concentrations as low as 100-1000 ppm VOC are possible.⁹ The size of the particulates in a waste stream which can be handled by an agitated thin film evaporator is limited by the clearance of the agitating blades and vessel surface, typically 1-3 mm (0.03-.1 in.). Streams having viscosities up to 100 poises have been treated. Consequently, thin film evaporators appear to be strong candidates for VOC removal from waste streams that lie between free-flowing liquids and viscous sludges. Care must be taken, however, against processing reactive organic streams which may polymerize at the evaporator's elevated temperatures.

Distillation

Distillation can be used to remove VOCs from free-flowing liquid wastes. While distillation is more frequently used to separate components of organic streams, it is used by waste recyclers to remove organics from mixed streams as well. Distillation has the advantage over steam stripping of not adding additional water to the system being treated. However, it cannot treat streams which are viscous or have a high degree of solids content, because these streams can foul the evaporation coils and the fractionation column plates. Distillation apparatus is more complex than batch steam strippers and requires more highly skilled personnel for operation.² Like steam strippers, it is energy intensive, requiring 50-2,500 kJ/kg (250-1,200 Btu/lb) of waste feed.

Other Techniques

For aqueous streams containing VOCs, several other treatment options exist. The ones which appear to be most promising to emissions control are (1) carbon adsorption, (2) wet air oxidation, and (3) ozonation/UV radiation. These techniques are all currently being used to varying degrees in wastewater treatment.^{2,10,11} Only carbon adsorption has been extensively used in hazardous waste treatment, and there has been little application of ozonation/UV radiation, except in cleanup of disposal site leachates. Wet oxidation has also only seen limited application in hazardous waste treatment.² These three techniques are not specific to volatiles removal from hazardous waste streams and other nonvolatile or slightly volatile stream constituents may compete with the process dynamics. Carbon adsorption is of

particularly limited applicability to a VOC removal program because there can be only limited suspended solids (<50 ppm) or oils and grease (<10 ppm) in the stream. (Some streams may, however, be pretreated by filtering or centrifugation to minimize fouling of the carbon.) Also the carbon must be regenerated, adding to the expense of treatment. Both wet oxidation and oxidation/UV radiation are limited in terms of the volatile species which they can destroy. For example, wet oxidation will not readily decompose highly chlorinated organics. While both techniques potentially result in the complete oxidation of treated compounds to water and carbon dioxide, in practice this does not always occur.² Some volatiles may be removed to only a very limited degree and in the process new volatile species may be produced.

Treatment of Hazardous Waste Sludges

Many industrial production processes result in hazardous sludges. These include distillation bottoms, filter cake, and various sludges and slurries of process byproducts.¹²

Treatment of hazardous sludge streams to remove volatile organics requires a different process or different process operating conditions than for liquid streams, mainly because the high solids mass clogs the reaction or adsorption interface used in liquid processes, fouls heating lines, and/or reduces mass transfer rates.

There are a number of sludge treatment techniques which are currently used in the disposal or recycling of municipal and industrial sludges. Municipal sludges are disposed of by incineration, composting, landfarming, or landfilling. Dewatering (e.g., evaporation or centrifugation) and stabilization are frequently used to prepare sludges for disposal.¹³ Treatment techniques for industrial sludges include incineration, wet oxidation, land treatment, and chemical fixation/stabilization/encapsulation.¹² Of these techniques, only evaporation is applicable to the narrow problem of VOC removal; with the exception of centrifugation, the other techniques are for ultimate disposal or involve reactions which change more than just the VOC content of the waste. Steam stripping should also be applicable.

Evaporation

Evaporative removal of VOCs from sludges will have the same advantages and disadvantages mentioned above for air stripping, except that it will be more costly, due to the need for thermal energy and waste mixing. For example, a sludge treatment system might consist of a steam-jacketed mixer/evaporator and an activated carbon adsorber/regenerator. For a system designed to handle 24 Mg (24 tons) of sludge per day, the steam is estimated to account for 35 percent of the annual operating costs.² The evaporator accounted for 50 percent of the equipment capital costs.² The additional water which would be generated from many sludges during evaporation would further increase costs due to the need for additional condenser capacity on the carbon adsorption system. Controls may also be required to remove particulates emitted from the dry product.

Stripping

A second system for VOC removal is steam stripping. It has been suggested that the waste could be circulated through a pipe with an auger which was perforated. Thus, both sludge mixing and steam sparging would be accomplished.¹⁴ Steam stripping of sludge has the advantage of providing more intimate contact between the steam/air mixture than does evaporation. In addition, steam stripping does not result in dewatering of the sludge, thus leaving the treated sludge amenable to further processing. As with steam stripping of liquids, this approach to VOC removal from sludges will require cleanup of the aqueous condensate and proper disposal of stripped organics.

Extent of Waste Treatment

The extent to which waste streams can be treated or currently are treated is influenced by several factors. As discussed in the section on system costs, the economic value of recovered organics usually dictates the extent to which recyclers treat a waste. This generally results in the bottoms being left with several percent organics. Technical considerations also limit the degree of treatment in recycling operations, however. Maximum temperatures in thin film evaporation may be set by the desire to avoid decomposition or reactions in the waste. In some instances, a requirement for an acceptable Btu value of thin film evaporator bottoms will limit the degree of low boilers if the bottoms are to be sold as fuel.

Recyclers use both stripping and distillation to achieve much lower organic concentrations than would be dictated by market considerations. In these cases, local regulations for waste disposal dictate the lower organic content. Steam stripping is currently used by one waste recycler to clean aqueous wastes sufficiently to be acceptable for discharge to the local wastewater treatment facility. A reduction in organic content to 0.1 percent is required. Similar requirements for aqueous waste disposal are met by other recyclers using fractional distillation.

At one waste management facility, wastes which initially contain 1-3 percent organics are stripped in preparation for disposal in an evaporation pond. In this situation, local air pollution permit requires that the concentration of organics in the vapor phase above the pond be less than 300 ppm.

Modeling of Pretreatment Processes

Models of treatment processes are needed for evaluating the process requirements for removing VOCs from each waste. Design parameters such as operating temperatures, residence time, steam rates, and number of theoretical trays needed for separations can be estimated by mathematical models in some cases without the need for expensive laboratory testing. Models are also useful for estimating parameters associated with the use of treatment for air emissions control, such as cost per unit volume of waste to achieve a specified level of volatile content, and the incremental cost effectiveness for volatile concentration reduction.

Models can be used to size the equipment needed to carry out the VOC removal. Flowsheet simulation software such as ASPEN (Advanced System for Process Engineering) can perform the material and energy balances necessary to describe a given process and can determine required residence times for

individual equipment items. Information of this type then is used by the model in equipment sizing and costing routines. If desired by the user, built-in optimization algorithms can be employed to manipulate process operating parameters in an effort to maximize performance and/or minimize total cost.

When field data are available for specific processes, the models permit an extrapolation of operation parameters to those required for greater VOC removal. Field testing of a batch, direct injection steam stripper indicated that the removal mechanisms was a first-order process.¹⁵ Then the logarithm of the concentration of each VOC in the batch waste being treated should be linear with time. The determination of the slope and intercept of the linear relationship will permit an estimation of the time (and cost) to achieve a specified concentration.

Models can be used to scale a treatment process up from a bench or pilot scale to plant scale. Factors such as column heat losses can be accounted for by geometrical similarity in the design of pilot scale equipment.¹⁶ The design liquid and gas flow rates in a distillation column can be used to estimate the height of packing in a packed column, after the number of theoretical stages is verified in pilot scale equipment.

Models can be used for process optimization to reduce the treatment cost or to permit a greater removal effectiveness of the process. One method of optimization involves the formulation of equations describing the desired optimization criteria (such as removal effectiveness, cost). The equations are then mathematically manipulated and the desired process parameters are calculated. The other method of optimization depends on a manipulation of the variables in an experimental program. The experimental program is desirable when equations are not available, and data to obtain the equations would be prohibitively expensive.

Types of Models Available

There have been many models proposed for separation technologies such as steam stripping, distillation, air stripping, and thin film evaporators.^{17,18} The basic model for each of the above processes is based upon thermodynamic equilibrium partitioning of the volatile material between two phases. The detailed models consider not only the thermodynamic equilibrium, but also the kinetics of mass transfer, heat transfer, and any reactions. In addition, the distribution effects (back-mixing) can be important.

One recent publication¹⁶ describes the procedures that a process development group at Polaroid Corporation used to design distillation processes. They merged the waste treatment process development with the process development for product synthesis. The waste treatment process was designed using vapor-liquid equilibrium data from the Dortmund Data Bank and calculating the theoretical performance of a distillation column. Pilot plant units were then used to confirm the predictions of the models.¹⁶ The models available for separation technologies are described in Perry's Chemical Engineers Handbook, McGraw-Hill, 1984, as well as standard chemical engineering textbooks.^{17,18}

Solvent extraction can be used to extract water soluble volatiles from water. The volatiles can then be removed from the solvent and the water easily stripped of the solvent. The data bases to support liquid-liquid equilibria are generally less extensive than liquid-vapor equilibria.

Laboratory equipment such as separatory funnels can be used to generate the required equilibrium data, using techniques such as those recommended by Treybal.¹⁹ In addition, Tierney's method^{24,25} is adaptable to modeling solvent extraction processes.

In the case of air stripping, the key information needed to design a tower (either with packed-bed or tray internals) for a specific waste treatment application is the equilibrium partitioning behavior of the VOC species between air and liquid phases. Unfortunately, such data are not available for many VOC-contaminated waste streams of interest, often forcing crude estimates that preclude reliable system optimization.

Four distinct types of mathematical solution techniques are available for predictive or evaluative aeration process modeling: graphical procedures, methods involving mass transfer coefficients, the overall "absorption factor" approach, and tray-by-tray calculations. Graphical procedures are adequate for the stripping of single components, but become tedious with multiple components because of the trial-and-error nature of the approach. Secondly, models based on the two-resistance theory of Whitman²⁰ typically define an overall mass transfer coefficient by combining the individual film resistances into a total resistance to interphase mass transfer. An excellent example of this type of model is the correlation developed for packed towers by Onda et al.²¹, which allows direct calculation of the film mass transfer coefficients (for a specified packing geometry and set of operating conditions) needed to determine an overall coefficient based on the liquid-phase concentration driving force. Thirdly, the "absorption factor" approach, developed by Kremser²² is a sometimes useful "short cut" method that sacrifices accuracy for speed but which should be useful for preliminary process feasibility studies.

The final type of mathematical model, direct tray-by-tray calculations for plate towers, involves the solution of the individual tray material and energy balances for the component flows on each tray. Starting with assumed vapor rate and temperature profiles, the lack of closure in the tray energy balances can be used to iteratively correct the vapor rate and temperature values, usually by a Newton-Raphson-type procedure. The method of Sujata,²³ which employs the above approach, has been used successfully for estimating the performance of multicomponent light-hydrocarbon absorption columns and would therefore probably be applicable for predicting VOC air stripping performance. It is also likely that similar matrix techniques currently used for distillation modeling (e.g. Tierney's Method,^{24,25} Naphtali-Sandholm Method,²⁶ Theta Method²⁷) could be adapted quite readily to air stripping.

One of the primary limitations of the use of models to predict the performance of separation processes is the absence of quality waste characterization data. Unless the waste characteristics are known, including VOC concentrations, amount of sludges, type of sludges and oils, and the presence of tars and polymerizable organics, it is difficult to accurately predict the requirements of separation equipment. The presence of some tars and solids could prevent the use of some of the techniques.

For multicomponent waste systems, the critical element in each of the separation process models is the equilibrium partitioning among the various phases. Although the partition coefficients can be estimated or obtained from the literature,^{28,29} laboratory verification is needed for many systems of interest. In the case of steam stripping and evaporation, the partitioning of a VOC between the gas and liquid phases is sometimes estimated using the ratio

of the pure component vapor pressure to the solubility. Although this may be a reasonable estimating procedure for very dilute pure components in water, it is inappropriate for many waste streams of interest. Preliminary analysis of field test data indicates that the rate of stripping may be overestimated by as much as two orders of magnitude by using the partitioning predictions based on pure component vapor pressure and solubility.¹⁵ Laboratory data characterizing component partitioning is therefore currently needed to predict the effectiveness of treatment equipment. Solvent recyclers have laboratory equipment such as a simple batch still to evaluate the vapor composition. Onsite treatment processes are also developed using pilot or bench scale equipment to verify the performance of the treatment technique. Experimental data are often needed for modeling the behavior of complex systems containing impurities.¹⁶

As new waste treatment technologies are developed to treat waste materials, there is generally not sufficient information to completely characterize the process models. Only when a technology is mature and has been operated with different types of wastes for an extended period of time on plant scale can accurate, dependable models be developed. In new technology development it is often useful to rely on statistical techniques for process analysis and optimization.³⁰

Established analytical techniques based on GC headspace analysis are adequate for determining ideal solution partitioning behavior. The widely used EPICS³¹ (Equilibrium Partitioning in Closed Systems) and batch air stripping methods³² can be used to yield values for Henry's constant which, when coupled with appropriate activity coefficient models, give an accurate and useful phase equilibrium representation. Experimental Henry's constant and activity coefficient data can be used to develop a correlation useful for predicting vapor liquid equilibrium (VLE) behavior from a knowledge of the chemical structure of the volatile components.³³ Recent studies indicate that the activity coefficient for phenol in the phenol-water system can be represented adequately by the existing van Laar model. Work is ongoing to evaluate the effect of VOC chemical structure on the experimentally determined Henry's constant.

Location of Treatment in Waste Management Cycle

There are a number of factors to consider in deciding at what point between generation of a waste and its ultimate disposal treatment for volatiles removal should occur. The appropriate location may vary depending upon the stream type and how it will be processed.

Treatment of hazardous waste should be carried out before the waste is exposed to conditions permitting significant air emissions. The sooner that the volatiles are removed from the waste after generation, the less the opportunities for the waste to be a source of air emissions.

Waste treatment to remove volatile components can be practiced as a part of the process which generates the waste in a dedicated treatment facility at the site of generation, or possibly even in equipment sometimes used for other purposes. Generally, waste streams of high volume can be treated on site in a more cost effective manner than shipping the waste to a waste management facility. If the recovered volatiles can be recycled onsite there are additional incentives. For the special case of dilute aqueous waste streams

which can be biologically treated, onsite pretreatment is often necessary because of the sensitivity of biological systems to specific wastes.

Waste material sometimes contains confidential specialty materials. For such a waste, the preferred method of waste disposal would generally involve onsite treatment. The mixing of various types of waste before shipping to a commercial treatment facility can cause treatment problems, since additional multiple distillation columns could be required to separate the various components. The cost of a simple distillation is approximately \$0.21 per liter, but multiple steps can increase the cost to \$0.70 per liter.³⁴

Another advantage for treating a stream at or near the point of generation is that pollutant concentrations are often greater in a concentrated stream than in a mixed waste material collected from various waste generation processes. The concentrated waste material is not only easier to strip, but also the recovered volatile material could require substantially less purification before recycle.

The point at which treatment is used may dictate whether batch, semi-batch or continuous treatment is used, depending on the volumes of wastes being handled. This in turn will influence what kinds of treatment processes can be used. Treatment at point of generation may use dedicated continuous or semicontinuous treatment processes, even though the unit may be small. At an offsite facility, different batches of wastes will generally be received and batch operations, such as are used by waste recyclers, will be most common. Techniques such as air stripping are best run as continuous processes, since this minimizes the possibility of offgas vapor concentrations drifting into the explosive range with batch processing. With biological treatment continuous processes are desirable since the process would tend to be more stable as the different wastes are blended before introduction to the process and step changes in concentration are avoided. Equalization will moderate the concentration surges. If batch treatment is required, steam stripping may be the preferred alternative.

System Costs

The processes that are likely to be used to treat wastes for VOC control are widely used in other industries. The treatment costs in their conventional use should generally provide a minimum cost figure for hazardous waste treatment. Three factors will influence the additional costs that will have to be incurred: (1) waste preparation prior to treatment, (2) increased maintenance, (3) different degrees of treatment, and (4) residuals disposal.

Waste may have to undergo pretreatment prior to treatment for VOC removal. While some treatment techniques, such as thin film evaporation, can handle solids in concentrations over a few hundred parts per million, others cannot. Fractional distillation units with heat exchange coils in their evaporators will foul if concentrations of dissolved or suspended solids are high in the incoming waste stream. In such cases, pretreatment to remove solids (e.g., through filtration or chemical precipitation) will be required. Even thin film evaporators are limited in terms of the amount of solids and/or viscosity of the wastes which they will accept. Addition of waste oil as a lubricant may increase the range of streams that could be handled by these units.

It is expected there will be increased maintenance costs associated with hazardous waste treatment due to the variability of waste stream composition. Increased maintenance costs are least likely to be a problem for continuous

processes, such as those that might be found at onsite treatment. For batch processes, similar to those found at hazardous waste recycling firms, costs increase because waste compositions vary daily. These maintenance costs can be expected to vary from process to process and facility to facility, but an operator should consider them when choosing equipment. For instance, the use of a thin film evaporator with external bearings will reduce the likelihood of frequent bearing replacement which has been observed at some hazardous waste treatment facilities utilizing internal bearings.³⁵

One of the potential increases in cost for VOC removal over the cost of conventional operation of these treatment techniques will be due to the increased degree of treatment that may be required. When a waste is recycled, the degree of treatment which is dictated principally by product resale credits and residual disposal costs. Often, only 80 percent of the recyclable organics are removed. More extensive treatment may be required in a VOC emissions control program. This will result in increased operating costs and, potentially, in increased capital costs. For example, consider a steam stripping system (Table 1). The initial concentration is 5 percent organic dissolved in water, and the waste is sparged with steam. The rate of reduction in organic concentration is assumed to be first order with respect to concentration and to exhibit a time constant of 30 minutes. For this system, 40 minutes typically might be required for batch charging, discharging, and heating.

Table 2 presents the variation in treatment costs as a function of the degree of waste treatment that is desired. This table shows that if only 80 percent of the VOC needs to be removed, the optimal cost-effectiveness of the system will be obtained; i.e., the amount of waste which can be handled annually for the smallest unit cost of VOC removal is 2.1 Gg. This cost minimum occurs because of the fixed downtime between batches and can be a major factor in determining the extent to which a recycler would operate the stripper for recovery of resalable product. If further VOC removal is required, the unit removal cost increases, primarily due to the increased retention times in the still. The incremental cost-effectiveness is a useful calculation, since it is an indication of the cost of removing additional volatile material due to the longer batch times. This somewhat simplified analysis suggests that there is little economic incentive to achieve very low levels of volatile materials unless there is specification of the maximum acceptable volatile content of the waste to be disposed.

This example shows that, while this steam stripping unit could handle 2.1 Gg per year for a solvent recycler, it could handle only 1.2 Gg per year if there is a limit of 0.1 percent VOC in the waste stream. In other words, the capacity of the steam stripper would have to be approximately doubled in order to handle the same waste load as handled by a recycler. Assuming that the capital costs of a process unit vary as the unit size raised to the 0.6 power, the capital investment for a VOC removal unit that could handle the same load as a conventional system will be 50 percent higher.

VOC Emission Reduction Costs

In many cases, the unit cost of treating a waste (\$/kg VOC removed) will not be equal to the cost of VOC emission reductions (\$/kg VOC controlled). VOC removal costs will be equal to or less than VOC emissions reduction costs. The relationship between these two unit costs is given by:

$$c(R) = c(T)/f$$

where $c(R)$ and $c(T)$ are the unit emissions reduction and treatment costs, respectively, and f is the fraction of VOCs that escape from the waste stream during waste management. For example, if the emissions source is a holding lagoon and the waste residence time is long, $f = 1$ and $c(R) = c(T)$. The same will be true if the emissions source is a landfill. On the other hand, if the principal emissions source is a neutralization lagoon with a short residence time, f may only be 0.2 to 0.5 and the unit cost of emissions reduction will be two to five times higher than the unit cost of waste treatment for VOC removal.

Treatment Residuals

The treatment of wastes for VOC removal can itself result in air emissions and other residuals which must be disposed of properly. Sources of air emissions from waste treatment will include process vents, waste transfer lines, storage tanks, wastes handling and spills. Liquid wastes will include contaminated cooling waters and scrubber streams, while solid residuals will result from such process emissions controls as carbon adsorbers.

In a steam stripping system, emissions will occur from working losses of influent and effluent storage tanks and from condenser and decanter vents (Figure 2). In some facilities, decanters either have no tops or have loosely fitting lids; improved seals may be required to ensure adequate worker and environmental protection. Condensers are found on steam stripping processes, as well as thin film evaporators and fractional distillation columns. Possible emissions controls for condenser vents include an auxiliary condenser, multiple passes through the evaporator, and inspection and maintenance and repair of leaks. An external control device such as a wash oil scrubber or a carbon adsorption unit could be employed, but in such cases costs of proper disposal of control residuals will have to be borne by the facility.

Air emissions from most waste treatment processes are expected to generally be much less than the amount of VOCs recovered. However, care must be taken to minimize system malfunctions which can result in increased air emissions. Condenser cooling water failure would result in significant increases in condenser vent emissions. Similarly, emissions could be expected to increase on thin film evaporators that are operated under vacuum if the condenser is overloaded. In addition, more stringent inspection and maintenance programs may have to be required for hazardous waste treatment facilities, since there is not the same economic incentive to minimize "product" loss that is found at manufacturing plants.

A number of hazardous waste management facilities dispose of their air emissions residuals through thermal combustion. At large facilities, a trunk line is used to route offgases to the air intake of boilers or waste incinerators. Smaller facilities flare their offgases. Recent studies have shown that combustion of wastes in boilers, cement kilns, and incinerators results in adequate (i.e., over 99.99 percent) destruction of organics as long as combustion temperatures are maintained above 1,000° C (1800° F). Flares have been shown to work effectively for organics destruction at petroleum refineries, but their efficiencies in destroying the complex mixtures of offgases from hazardous waste facilities is unknown. Of particular potential

concern is the destruction efficiency of flares for halogenated organics, which are not as combustible as other organics.

Few solid or liquid residual streams are produced as ancillary products to the treatment processes discussed. Table 3 indicates such streams for a number of potential VOC removal processes. One of the major liquid waste streams is steam condensate from sparged steam stripping processes. This can often be recycled with the incoming waste, thus reducing the volume of water residual byproduct. Unlike recycling operations, where there is often a solid or liquid residual from physical separation processes (i.e., the "bottoms"), this stream will be the waste that has been treated for VOC removal.

Conclusions

1. There are a number of treatment techniques potentially applicable to VOC removal from waste streams. These techniques include steam stripping, air stripping, distillation, and thin film evaporation.
2. The applicability of many of these techniques has been commercially established at recycling firms for the treatment of VOC-containing waste streams.
3. Models are available for each of the common VOC removal waste treatment processes. Waste characterization data will be needed to apply these models to specific systems of interest.
4. The incremental cost of removing VOCs increases rapidly as low concentrations of VOCs are attained.
5. Some types of hazardous wastes are difficult to treat with conventional technologies. Out of specification products such as incompletely reacted polyurethane foam are not amenable to conventional pretreatment technologies.
6. Relatively little commercial experience has been obtained for the pretreatment of material for which there is little solvent recovery credit, such as sludges with low VOC concentrations (<1 percent).

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TABLE I. EXAMPLE STRIPPER PROCESS DESIGN PARAMETERS AND WASTE STREAM CHARACTERISTICS

<u>Design Parameters</u>	
Process type	Batch operated, sparged steam stripping
System capacity	1,900 liters (500 gal.)
Thermal load	200 kg steam/hr (440 lb/hr)
<u>Waste Stream Characteristics</u>	
Batch volume	546 l (150 gal.)
Composition	
Water	95 percent
VOCs	5 percent
Density	1.0
Stripping time constant	30 min.

TABLE II. COST-EFFECTIVENESS OF EXAMPLE STEAM STRIPPING SYSTEM^a

Residual volatile in waste, %	3	1	0.5	0.25	0.1	0.05	0.025
VOC removed, liter	11	23	25	27	28	28	28
Batch cycle time, min. ^b	55	88	109	130	157	178	199
Annualized waste amount, Gg	3.4	2.1	1.7	1.5	1.2	1.1	0.95
Annualized VOC removed, Mg	69	86	78	69	59	53	47
Total Annual Operating Cost ^c , K\$	300	300	300	300	300	300	300
Cost per unit volume:							
Waste treatment, \$/liter	0.09	0.14	0.17	0.21	0.25	0.28	0.31
VOC removed, \$/liter	4.38	3.49	3.84	4.33	5.88	5.78	6.33
Incremental cost, \$/liter VOC removed	4.38	2.61	6.58	13.17	29.01	65.84	131.68

^a See Table 2 for engineering design and waste characteristics.

^b 40 minutes plus length of steam stripping.

^c Includes operating cost, capital depreciation, and interest (Reference 9).

TABLE III. TREATMENT PROCESS RESIDUALS

Process	Air ^a	Water ^b	Solids ^b
Agitated Thin Film Evaporation	- Condenser vents - Vacuum pumps	- Contaminated cooling water	-
Batch Steam Stripper	- Condenser vents	- Contaminated cooling water - Steam condensate	-
Steam Stripping	- Process air	-	-
Fractional Distillation	- Condenser vents - Vent pumps	- Contaminated cooling water	-
Carbon Adsorption/Regeneration	- Regeneration furnace	- Reacted carbon transport water	Spent carbon
Wet Air Oxidation	- Excess process vapors - Process offgas	- Contaminated process cooling water	Catalyst residue
Ozonation/UV Radiation			-

^aWill include storage tank vents, as well as transfer line flanges, valves, pumps, etc. for all processes.^bMay include waste solids and wastewaters from filtering to remove solids prior to treatment for VOC removal.

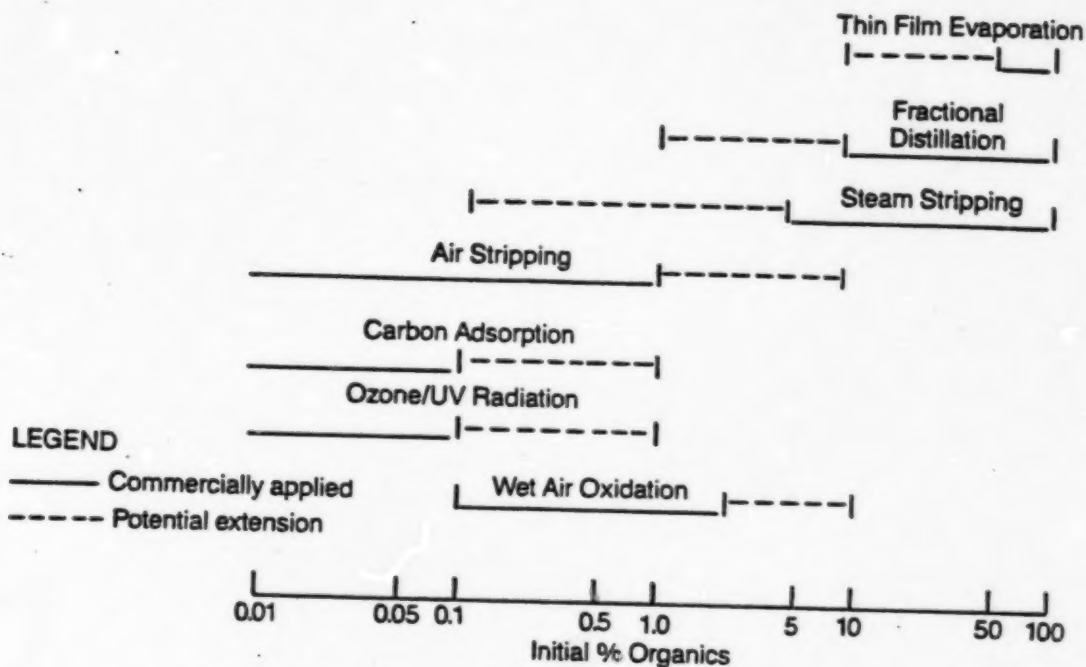


Figure 1. Approximate Ranges of Applicability of VOC Removal Techniques as a Function of Organic Concentration in Liquid Waste Stream.

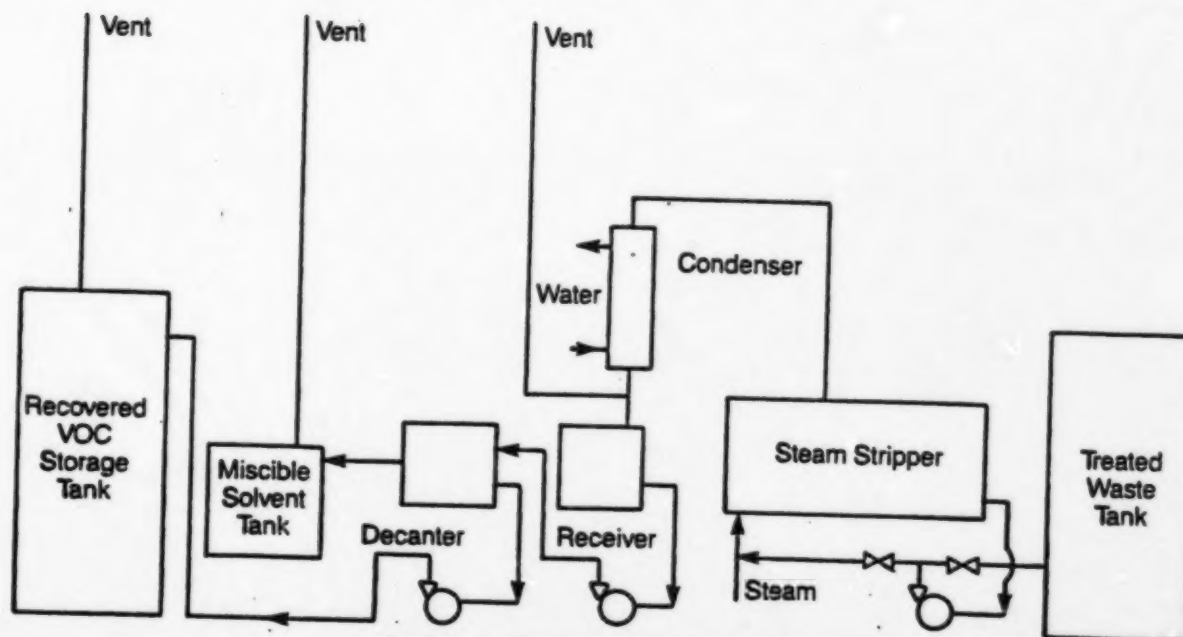


Figure 2. Batch Steam Stripping Process.